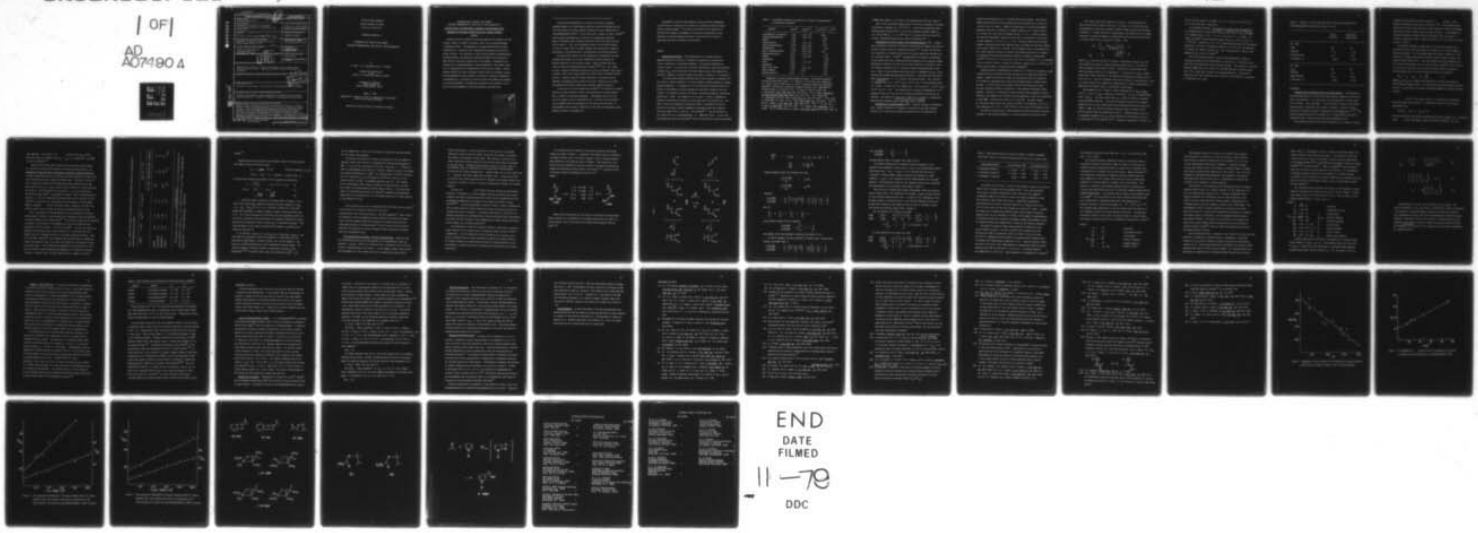
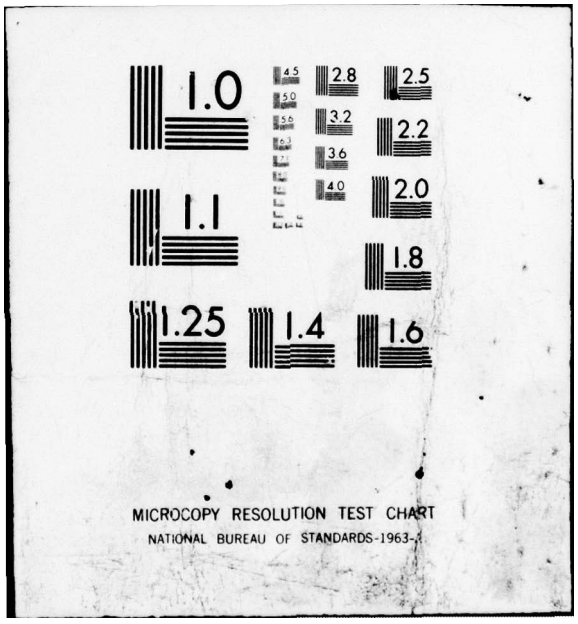
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Quantum yields are reported for the photoaddition of biacetyl, a ketone having a visible absorbing chromophore, and a series of alkenes in benzene solution. Biacetyl phosphorescence quenching and quantum yield data are consistent with a photoaddition mechanism involving biacetyl triplets. Exciplex and biradical intermediates are proposed for photoaddition on the basis of stereochemical results and the dependence of phosphorescence quenching constants on electron donor properties of alkenes. The consequence of utilizing low energy excited states in small ring forming addition reactions is discussed.

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PHOTOADDITION OF BIACETYL AND ALKENES

REACTION STEREOCHEMISTRY, MULTIPLICITY, AND PHOTOKINETICS

by

G. Jones, II, M. Santhanam, and S.-H. Chiang

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PHOTOADDITION OF BIACETYL AND ALKENES
REACTION STEREOCHEMISTRY, MULTIPLICITY, AND PHOTOKINETICS

Guilford Jones, II* Mahalingham Santhanam, and Sheau-Hwa Chiang
Department of Chemistry, Boston University, Boston, MA 02215

ABSTRACT

Quantum yields are reported for the photoaddition of biacetyl with the alkenes, indene, 2,3-dimethyl-2-butene, furan, and 1,2-dimethoxyethene in benzene solution. The dependence of quantum efficiencies on alkene concentration is consistent with a photoaddition mechanism involving biacetyl triplets. The quenching of fluid solution biacetyl phosphorescence has been observed, and quenching constants correlate with the electron donor ability (ionization potentials) of the alkenes. Photoaddition of biacetyl and 1,2-dimethoxyethene is non-stereospecific, and oxetane formation is accompanied by the isomerization of the starting alkene. Stereochemical results are used to estimate relative rates of cleavage, closure, and stereorandomizing bond rotation in biradicals, proposed intermediates in photoaddition. Exciplexes of triplet biacetyl and alkenes are proposed as primary photochemical intermediates (precursors to biradicals) on the basis of the stereochemical, emission quenching, and other data.

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The solution photochemistry of biacetyl and related dicarbonyl compounds appears to be dominated by reactions involving hydrogen abstraction from solvent or another reagent followed by various combinations of the photogenerated radicals.[1] On the other hand, a number of recent reports[2,3] have described photoaddition of biacetyl and unsaturated substrates under circumstances where hydrogen abstraction might have taken place but did not prevail. Thus, the conjugated dicarbonyl functionality appears to join the larger class of simple alkanones and alkanals which readily participate in the Paterno-Buchi (cycloaddition) and related reactions.[4]

The quantitative aspects of this comparison of dicarbonyls and other aldehydes and ketones are not well understood, and the mechanism of biacetyl addition is only partially known. Several alkenes have been shown to quench the phosphorescence of biacetyl,[2a,d,e] but in a number of cases biacetyl fluorescence emission can also be quenched[5]. These results in general permit that either singlet or triplet states of biacetyl may be reactive. Labeling studies[2a] further show that 1,4 biradicals may be important intermediates which follow the initial interaction of biacetyl and quenchers and lead to oxetane and "ene-type" addition products.

In the spirit of earlier mechanistic analyses[4,6] of alkanone and alkanal addition, we have examined in detail the interaction of excited biacetyl with a variety of unsaturated compounds. Luminescence results and the profile of quantum yield of photoaddition as a function of the concentration of addends allow the assignment of the reactive excited state. A stereochemical test provides information on the nature of penultimate intermediates involved in photoaddition.

Cycloaddition reactions which employ visible absorbing chromophores as sensitizers or substrates are currently of interest as means for photochemical energy storage.[7] The results for biacetyl allow comparison of more and less energetic chromophores, giving some understanding of what penalties in rate and quantum efficiency of reaction are to be paid in deploying relatively low energy excited species.

RESULTS

Luminescence Quenching. The phosphorescence of nitrogen purged or degassed solutions of biacetyl in benzene was quenched with varying efficiency on addition of unsaturated compounds. The quenchers employed are listed in Table 1 (including data from other laboratories) along with quenching constants ($k_q\tau_0$ values) obtained from Stern-Volmer analysis and computed rate constants, assuming a reported lifetime for biacetyl triplets (τ_0 = 0.46 msec).[8]

The relationship between quenching rate and the structure of quenchers did not reveal an obvious dependence on either quencher triplet energies or hydrogen donating properties. A reasonable fit of the data with the electron donor properties of the alkenes and other quenchers was obtained as shown in the plot (Figure 1) of quenching constants and alkene ionization potentials (correlation coefficient = 0.939). Two quenchers (not included in Figure 1) appeared exceptional with quenching constants falling above the IP correlation line. The higher rate for 2,5-dimethyl-2,4-hexadiene (DMH) is consistent with the imposition of an energy transfer component to quenching, given the relatively low lying triplet level for DMH ($E_T \leq$ 56 kcal/mol[9]).[10] Such an artifact is less likely for cis-1,2-dimethoxyethene (c - DME)(vide infra). In this case the problem may involve the reported[12] value for the vertical ionization potential

Table 1. Stern-Volmer Constants for Quenching of Biacetyl Phosphorescence by Unsaturated Compounds[a]

Quencher	IP_V(eV)[b]	$k_q\tau_o$ (M^{-1})	k_q ($M^{-1}sec^{-1}$, x 10^{-5})
2,5-dimethyl-2,4-hexadiene	7.84[c]	3.66×10^5	7960.
hexamethyldewarbenzene	7.90[d]	1.04×10^3	22.6
indole	7.92[e]	--	129.[j]
N-methylpyrrole	7.95[f]	1.25×10^3	27.2
trans-1-phenylpropene	8.28[g]	4.84×10^2	10.5
dihydropyran	8.34	9.06×10^1	1.97
cis-1,2-dimethoxyethene	8.39[h]	4.30×10^4	935.
tetramethylethylene	8.42[i]	7.00×10^1	1.52
indene	8.63	1.24×10^2	2.70
cyclohexene	8.72	--	1.00[k]
furan	8.89	3.15×10^1	0.68
norbornene	8.95	--	0.24[l]
ethyl vinyl ether	9.07[h]	2.63×10^1	0.57
trans-2-hexene	9.16	4.60	0.10
methacrylonitrile	10.39	< 0.5	< 0.01

[a]Degassed or nitrogen purged benzene solutions. [b]Ionization potentials available except where noted: J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, and K. Draxl, and F.H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, National Bureau of Standards, 1969. [c]M. Beez, G. Bieri, H. Bock, and E. Heilbronner, Helv. Chim. Acta, 56, 1028 (1973). [d]G. N. Taylor, Zeitschrift fur Physikalische Chemie Neue Folge, 101, 237 (1976). [e]L.N. Domelsmith, L.L. Munchausen, and K.N. Houk, J. Am. Chem. Soc., 99, 4311 (1977). [f]A.D. Baker, D. Betteridge, N.R. Kemp, and R.E. Kirby, Anal. Chem., 42, 1064 (1970). [g]E.W. Fu and R.C. Dunbar, J. Am. Chem. Soc., 100, 2283 (1978). [h]Ref 12 [i]W. Fuss, and H. Bock, J. Chem. Phys., 61, 1613 (1974). [j]E. Fujimori, Mol. Photochem., 6, 91 (1974). [k]H.L.J. Backstrom and K. Sandros, Acta Chem. Scand. 14 48 (1960). [l]Ref. 2d.

of c-DME which appears to be slightly high compared with other enol ethers.[13]

Most of the unsaturated compounds were not efficient quenchers of biacetyl fluorescence in benzene ($k_q \leq 10^7$ $M^{-1}sec^{-1}$). Those with exceptionally good electron donor properties ($IP_v \leq 8.0$ eV) were moderate quenchers (DMH, k_q = 3.4×10^8 and NMP, k_q = 5.1×10^8 $M^{-1}sec^{-1}$), consistent with the results for biacetyl fluorescence quenching by alkenes in acetonitrile.[5]

Photoaddition to Furan, Indene, and Tetramethylethylene (TME). Preparative irradiation of biacetyl and furan or indene gave the oxetanes (BI-FUR and BI-IND) as major products as reported previously.[2b,c] Biacetyl and TME were not irradiated on a preparative scale but the major product was assumed to be the "ene-type" adduct , BI-TME[2b]. Quantum yields for biacetyl disappearance in the presence of furan, indene and TME were measured using a Rayonet chamber photoreactor equipped with lamps with principal emission at 330-390 nm. Plots of reciprocal quantum yield vs. reciprocal alkene concentration were linear (e.g., Figure 2) and intercept/slope ratios were in agreement with $k_q\tau_o$ values obtained from phosphorescence quenching (Table 1), consistent with the assignment of the biacetyl (n, π^*) triplet as the reactive state. Thus, the data for TME (Figure 2) resulted in i/s = 78 M^{-1} ($k_q\tau_o$ = 70 M^{-1}) and a limiting quantum yield, 1/i = 0.098. A similar plot for indene (0.02 - 0.10 M) gave i/s = 133 M^{-1} ($k_q\tau_o$ = 124 M^{-1}) and 1/i = 0.011. The quantum yield of biacetyl disappearance in the presence of furan was very low and a complete concentration profile was not obtained. The quantum efficiency was $\sim$ 0.005 at 0.1 M furan, a concentration where biacetyl phosphorescence quenching (but not fluorescence quenching) is nearly complete.

Photoaddition to Dimethoxyethene (DME). Biacetyl and cis-1,2-dimethoxyethene (c-DME) on photolysis in benzene or acetonitrile gave two principal products ($\sim$2:1) which were isolated by preparative glc and identified by

spectral and microanalysis as 1:1 biacetyl-DME oxetane adducts. Nmr analysis showed that these glc purified oxetanes were not homogeneous but in fact consisted of pairs of isomers. Oxetane ring hydrogens for the major photoadduct appeared as two pairs of doublets of unequal intensity (~5:1, larger signals at 3.8 and 5.0δ), both pairs of doublets having J = 3 Hz. A similar spectrum for the minor photoadduct revealed also two pairs of doublets for ring protons (larger component, 4.1 and 5.2 δ, J = 5 Hz). The major adducts were assigned epimeric structures having trans methoxy groups (t-BI-DME) and the minor adducts to the other isomeric pair, c-BI-DME. The assignment relies on the expectation of a higher coupling constant for oxetane ring protons which are cis oriented, a criterion which has been consistently applied to a number of stereoisomer pairs.[6,14] Verification of the criterion rests with the assignment of cis stereochemistry to the minor adduct of acetone and dimethyl maleate which is alternatively obtained from the adduct of acetone and maleic anhydride.[15]

Quantum yields for photoaddition of biacetyl as a function of [c-DME] followed a pattern which was different from that observed for the previously described systems. Between 0.001 and 0.01 M DME, the quantum efficiency for appearance of t-BI-DME was unchanged (about 0.05) but decreased sharply at higher concentrations. A similar result was obtained starting with biacetyl and t-DME. Two other important features of photolysis in the presence of DME were readily apparent. Geometrical isomerization of the starting alkene accompanied oxetane formation, was somewhat more efficient than cycloaddition, and was also suppressed at high [DME]. Starting with either cis or trans DME, the major oxetane was the trans isomeric pair; the ratio of t-BI-DME to c-BI-DME was $1.62 \pm 0.30 : 1$ from c-DME and $2.47 \pm 0.45 : 1$ from t-DME for a wide range of DME concentrations.

The addition quantum yield - DME concentration profile was readily analyzed assuming (1) that oxetane formation is a triplet reaction (2) that due to the

high rate of DME triplet quenching, relatively low concentrations of DME are sufficient to quench virtually all triplets, and (3) that very high concentrations of DME quench biacetyl singlets thereby reducing the efficiency of addition. If these constraints indeed operate, the quantum yield of product formation is simply the product of intersystem crossing yield and the fraction of triplets which lead to a particular product. Thus,

$$\phi_{PR} = \left(\frac{k_{isc}}{k_{isc} + k_q^1 [DME]} \right) \left(\phi_T \right) \qquad (1)$$

$$\frac{1}{\phi_{PR}} = \frac{1}{\phi_T} + \frac{k_q^1 [DME]}{k_{isc}\, \phi_T} \qquad (2)$$

where k_{isc} is the rate constant for biacetyl intersystem crossing, k_q^1 is the rate constant for biacetyl singlet quenching by DME, and ϕ_T is the inherent yield of product from biacetyl triplets. (Unimolecular singlet decay other than intersystem crossing is not important.[1b]) Curved plots of ϕ_{PR} vs 1/[DME] showed that singlet reactivity in cycloaddition and geometrical isomerization is quite low (i.e., from the intercepts, the quantum yields are, conservatively, < 0.01 for oxetane formation and geometrical isomerization at infinite concentration of [DME] where all biacetyl decay is bimolecular singlet decay).

Rearrangement of eqn 1 reveals a linear relationship of $1/\phi_{PR}$ and [DME] (eqn 2). A plot of $1/\phi_{PR}$ vs [DME] has an intercept = $1/\phi_T$ and a slope/intercept ratio = k_q^1/k_{isc}. The latter should equal $k_q\tau_o$, values for which are obtained from fluorescence quenching. Low conversion quantum yields of trans oxetane appearance and cis-trans isomerization were obtained starting with biacetyl and t-DME or c-DME; the resulting reciprocal plots are shown in Figure 3 and 4, and the important data are summarized in Table 2. Slope/intercept ratios are in reasonable agreement with $k_q\tau_o$ values obtained from fluorescence quenching by c-DME (30.6 M^{-1}) and t-DME (27.0 M^{-1}). Assuming a fluorescence lifetime (τ_o)

of 10.2 ns[5] for biacetyl in benzene, $k_q^1 = 3.0 \times 10^9$ and 2.6×10^9 $M^{-1}sec^{-1}$ for cis and trans DME, respectively.

An assessment was made of the effect of solvent on the rate and yield of cycloaddition for biacetyl and c-DME. From results of photolysis in acetonitrile, a linear plot of $1/\phi_{ox}$ (t-BI-DME) vs. [c-DME] yielded s = 317, i = 18, s/i = 18, and $1/i = \phi_T = 0.056$. The slope to intercept ratio compared favorably with $k_q\tau_o = 25$ M^{-1} and $k_q^1 = 3.1 \times 10^9$ $M^{-1}sec^{-1}$ (assuming $\tau_0 = 8.0$ ns[5] in acetonitrile, obtained from fluorescence quenching). The ratio of t-BI-DME/c-BI-DME was 2.18 $\pm$ 0.25 for the photolysis of biacetyl and c-DME in acetonitrile. The ct isomerization of DME was also observed but not studied in detail.[16]

The role of energy transfer in driving the isomerization of DME was evaluated by comparing the effectiveness of biacetyl (E_T = 56 kcal/mol) and a sensitizer with comparable triplet excitation energy. Thus, parallel irradiation (Rayonet 3000Å lamps, Pyrex tubes) of 0.01 M DME solutions, nitrogen purged and 0.2 M in sensitizers biacetyl and 2-acetonaphthone (E_T = 59 kcal/mol) showed that the latter sensitizer was at least 10x less effective in promoting ct isomerization of c-DME.

Table 2. Slope and Intercept Data from Plots of Reciprocal Quantum Yield and Dimethoxyethene Concentration (Figures 3 and 4)

	Oxetane Formation	Geometrical Isomerization
For c-DME		
slope	708	110
intercept	17.2	3.10
slope/intercept	41.1	35.6
1/intercept = ϕ_T	0.058	0.322
For t-DME		
slope	382	510
intercept	15.4	11.1
slope/intercept	24.8	45.9
1/intercept = ϕ_T	0.065	0.107

DISCUSSION

Phosphorescence Quenching; Biacetyl and Other Ketones. The dependence of emission quenching rate on the electron donor-acceptor properties of emitting species and quenchers is an increasingly routine observation in recent years and is relatively well understood.[17] The electrophilic nature of the excited carbonyl group in encounters with alkenes is apparent in profiles for the quenching of alkanone and alkanal fluorescence and phosphorescence.[4a,12,18] The electron accepting character of biacetyl (n,π^*) singlets[5,8] and triplets[8] on interaction with a variety of donors has been documented as well.

The uniformity with which the rate of quenching of n,π^* carbonyl emission

responds to the structure of alkene quenchers is striking. Data recently collected by Loutfy and his coworkers[18] for ketone phosphorescence quenching by alkenes along with data for the quenching of ketone fluorescence and values from our biacetyl study are shown in Table 3. The dependence of quenching constants on alkene ionization potential (from the slopes of IP plots, $\Delta \log k_q/\Delta IP$) shows a standard deviation of 0.3 eV^{-1} about an average value of -1.8 eV^{-1}.

The standard treatment of these data is to associate quenching rate constants with the free energy change for formation of an excited complex of ketone and quencher. The free energy change for exciplex formation is then treated as a binding energy which associates ketone (electron acceptor) and alkene (electron donor) pairs. This free energy of exciplex formation turns out to be (for the ketones, Table 3, and for other systems[20]) a small fraction (f_{ct} values) of the energy of an outright electron transfer from donor to excited acceptor which can be calculated from the Weller equation[21]

$$\Delta G_{ct} = E_{ox} - E_{red} - E_T - \frac{e^2}{\epsilon r} \qquad (3)$$

where E_{ox} and E_{red} are standard redox potentials for donor and acceptor in their electronic ground state, E_T is the excitation energy of ketone (acceptor) and $e^2/\epsilon r$ is the energy of coulombic attraction between fully charged exciplex partners.

In this "first order" analysis, the correlation of quenching data with alkene donor properties is understood in terms of the following proportionalities

$$\log k_q \propto \Delta G_{ct} \propto E_{ox} \propto IP_v$$

with the implication that factors associated with exciplex geometry (e.g. dependences on r), steric requirements, specific solvent interactions, etc, are

less important. For biacetyl, the portion of the ΔG_{ct} driving force excluding the coulombic term ($E_{ox} - E_{red} - E_T$) ranges from -0.14 (DMH) to 1.08 eV (2-hexene).[22]

Along with the rather smooth trends found for relative rate constants as a function of alkene donor properties, we have noted particularly the dependence of absolute rates of quenching on sensitizer (ketone) properties. In Table 4 quenching data for four ketones and three quenchers are shown along with excitation energy and reduction potential data. The central finding is that, although the ketone excited states should have essentially the same redox driving force ($E_T + E_{red}$), absolute rate constants for triplet quenching vary widely. The correlation of log k_q with ($E_T + E_{red}$) for quenching by TME which has been noted[18] is apparently fortuitous. Such a correlation would require $f_{ct} = 0.88$ (an interaction with donor having nearly complete electron transfer), a value which is inconsistent with the response of alkene donors. Notably, quenching data for the other alkenes, especially including the biacetyl results, do not follow the partially developed pattern for TME.

Thus, the quenching of the phosphorescence of one ketone with different alkenes shows a different structure-reactivity relationship than the quenching of several ketones with a single alkene.[24] The two-fold correlation for quenching by alkenes is reminiscent of the dependence of the rate of ketone triplet quenching on the IP of amines and similar donors[25] and the less regular dependence of amine quenching on ketone properties.[26] We believe that this behavior may be an important artifact of multistep quenching processes. Yang, Turro and their coworkers[4a] have suggested that the quenching of alkanone and alkanal fluorescence results from reversible formation of exciplexes followed by exciplex decay. This contention was supported by the observation of negligible or slightly negative temperature dependences of fluorescence quenching constants, a property which has been associated with a number of exciplex

Table 4. Ketone Triplet Energies and Reduction Potentials and Rate Constants for the Quenching of Ketone Phosphorescence by Alkenes

Ketone	E_T (eV)	E_{red}[a] (V)	$E_T + E_{red}$ (eV)	$k_q(M^{-1}\ sec^{-1}) \times 10^6$		
				enol ether	tetramethylethylene	norbornene
Acetone	3.38	-2.31	1.07	340[b]	51	43
Butyrophenone	3.13	-2.03	1.10		460	37
Benzophenone	2.94	-1.84	1.10	1100[b]	895	40
Biacetyl	2.42	-1.22	1.20	0.2[c]	0.15	0.024

[a]Polarographic half-wave reduction potentials (vs Ag/AgCl, CH_3CN) reported in ref 19. Value for biacetyl computed from reduction potential in DMSO ($E_{1/2}$ = -1.27 V vs SCE); G.A. Russell and S.A. Weiner, J. Am. Chem. Soc., 89, 6623 (1967). [b]1-Ethoxy-2-methylpropene. [c]Dihydropyran

systems.[20]

Reversible exciplex formation and nonradiative decay for triplet ketones and alkenes require the following steps

$$^3K + A \rightleftharpoons {}^3[K\text{--}A] \qquad \text{exciplex formation } k_1, k_{-1}, K_1$$

$$^3[K\text{--}A] \longrightarrow K + A + \text{products} \qquad \text{exciplex decay } k_2$$

for which the following relationships for the quenching constant apply

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} = K_1 k_2 \quad (\text{if } k_{-1} >> k_2) \qquad (4)$$

$$\log k_q = \log K + \log k_2 \qquad (5)$$

$$= -\frac{\Delta G_{exc}}{2.3\,RT} - \frac{\Delta G_{ed}^{\neq}}{2.3RT} \qquad (6)$$

A relatively smooth correlation of the type shown in Figure 1 is consistent with the kinetics scheme for reversible exciplex formation if $\Delta G_{exc} = f_{ct} \Delta G_{ct} - T\Delta S_{diff}$[27] and if k_2 is relatively insensitive to the donor properties of quenchers or shows a response to donor IP which parallels that of K_1. This latter coincidence of equilibrium and rate dependences would not be of help in explaining the wide variation in quenching constants for several ketones with one quencher (Table 4) (where ΔG_{ct} is relatively constant). This large variation is more readily associated with changes in k_2 which are not related to the donor IP.

If the formation constant for exciplexes can be understood in terms of the polarizability of carbonyl triplets and quenchers, on what then does the magnitude of $\Delta G_{ed}^{\neq}$ depend? Biacetyl triplets are a telling example in the profile of alkene quenching due to their diminished excitation energy. The relative slowness of biacetyl triplets in bimolecular reactions is well appreciated.[8,28] The deterant might signal the relationship $\Delta G_{ed}^{\neq} = f_{ed} E_T$

but the comparisons of Table 4 are not entirely supportive (acetone triplets are less robust than expected).

In the next section we will discuss the evidence for the involvement of biacetyl triplets and biradicals in photoaddition (and photoisomerization of DME). If k_2 is to be associated with the step, ^{3} exciplex $\longrightarrow$ ^{3}biradical, then the thermodynamics and kinetics of covalent linkage of biacetyl and alkene are important determinants of $\Delta G_{ed}^{\neq}$. The exothermicity of biradical formation will be a function of E_T and the energies of biradicals such as (for the ketone series) B1 and B2. An expected stability order (B1 << B2) coupled with the diminished triplet energy of biacetyl are qualitatively in accord with trends for phosphorescence quenching shown in Table 4. The delocalized nature of the non-bonding orbitals of biacetyl[30] (compared with monoketones) shares part of the responsibility for the reduced reactivity (a kinetic effect) of the dicarbonyl triplet.

Factors governing the rate of reversibly formed exciplexes may be complex.[31] A direct addition of carbonyl alkene pairs with polar characteristics, not involving biradicals, has been suggested.[32] Other factors not necessarily involving addition, include rotational and other motion away from an exciplex geometry which affect spin-orbit coupling and the rate of intersystem crossing to the ground state.[33] We will return to the structure-reactivity relationships for emission quenching after examination of quantum yield and stereochemical data.

The Triplet Route to Oxetanes. Biradical Intermediates. Quenching data and concentration profiles for the quantum yield of photoaddition (with one exception - biacetyl + DMH[34]) are consistent with a predominant role of biacetyl triplets in photoreduction with alkenes. For the addends, indene, TME and furan (and presumeably for other alkenes that are not exceptionally good electron

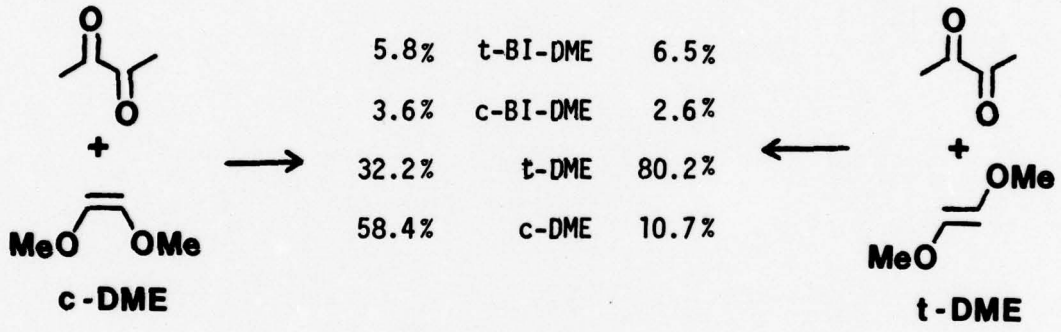
donors) the default of singlet reactivity is not the result of selective bimolecular singlet decay but simply a failure of the alkenes to intercept the shorter lived biacetyl excited state. DME provides a true test of biacetyl singlet and triplet reactivity since both excited states are quenched by the enol ether. Although triplet addition yields (1/i values, Table 4) are moderate, they are (conservatively) 5X larger than limiting quantum efficiencies for singlet photoaddition. Singlets appear not to play a major role in biacetyl sensitized isomerization of DME as well. A heavy restriction is placed on the triplet mechanism for this reaction since energy transfer from relatively low energy triplets is ruled out (comparison of biacetyl and acetonaphthone).

We share the view of others who have studied the sterochemical features of interaction of excited carbonyl triplets and alkenes that oxetane formation and alkene isomerization follow similar paths. Cycloaddition and the accompanying isomerization of alkenes or enol ethers by acetone or benzophenone[14b,35] have been understood in terms of triplet biradical intermediates which undergo significant stereorandomization before intersystem crossing and cleavage and closure to products. The general observation is partial but not complete convergence of stereochemistries starting with pure alkene stereoisomers, consistent with the findings for the isomerization of simple alkenes sensitized by aryl ketones via the Schenk mechanism.[36]

The stereochemical results for biacetyl addition to DME submit to detailed kinetic analysis if one assumes that all bimolecular decay involves biradical intermediates. For this mechanism biradical formation has a quantum yield of unity at concentrations of alkene sufficient to quench all biacetyl triplets. All product formation and quantum wasting return to starting materials result from biradical cleavage and closure (including bond rotations which mix stereochemistries).

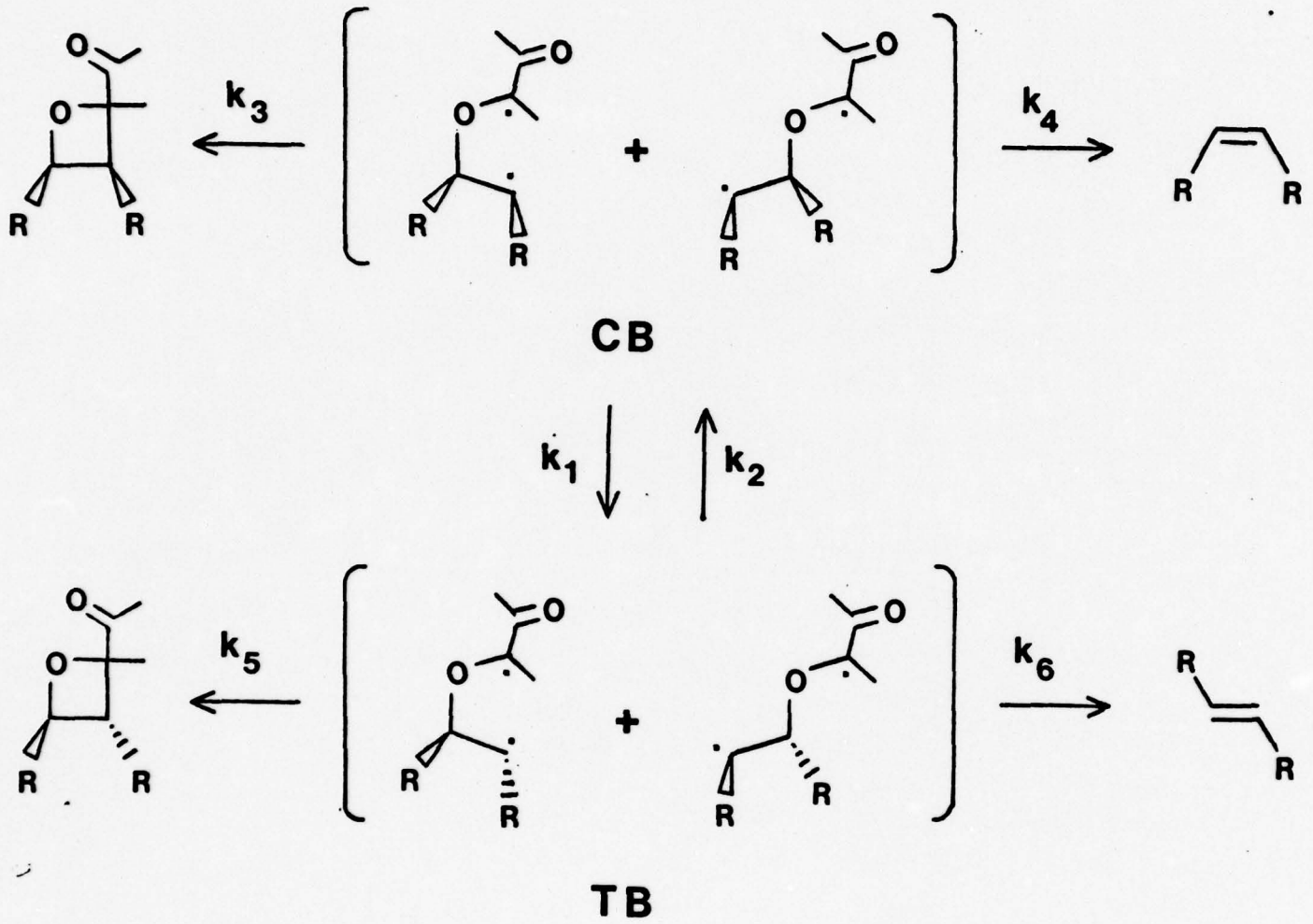
The limiting yields of products from (triplet) biacetyl and the DME isomers are shown in Scheme 1. Information from product ratios is sufficient to compute relative rates of biradical cleavage, closure, and bond rotation with reference to the processes shown in Scheme 2. Most helpful for this analysis was the treatment of data for biradicals resulting from diazene decomposition described by Dervan Uyehara, and Santilli,[37] a procedure similar to the early analysis by Montgomery and Bartlett.[38]

Scheme 1.



Steady state relationships for the family of biradicals have approximate gauche (nascent cis) stereochemistry for methoxy groups (CB) are readily derived assuming a start from biacetyl and t-DME (trans biradicals take the symbol TB).

Scheme 2



$$\frac{d(CB)}{dt} = k_2 (TB) - (k_1 + k_3 + k_4)\ (CB) = 0$$

$$\frac{(TB)}{(CB)} = \frac{k_1 + k_3 + k_4}{k_2}$$

Oxetane formation obeys the following rate laws.

$$\frac{d\ (c\text{-BI-DME})}{dt} = k_3\ (CB)$$

$$\frac{d\ (t\text{-BI-DME})}{dt} = k_5\ (TB)$$

Therefore

$$\frac{(t\text{-BI-DME})}{(c\text{-BI-DME})} = \frac{k_5}{k_2}\left(\frac{k_1 + k_3 + k_4}{k_3}\right) = \frac{k_5}{k_2}\left(\frac{k_1}{k_2} + \frac{k_4}{k_3} + 1\right)$$

Now let

$$\frac{k_5}{k_2} = W \quad \frac{k_3}{k_1} = X \quad \frac{k_4}{k_3} = Y \quad \frac{k_6}{k_5} = Z$$

We use three of these ratios to generate

$$\frac{(t\text{-BI-DME})}{(c\text{-BI-DME})} = W\left(\frac{1}{X} + Y + 1\right)$$

The oxetane ratio from experiment (starting from t-DME) is 2.47.

A similar treatment of trans biradicals at steady state, starting from biacetyl and α-DME leads to

$$\frac{(c\text{-BI-DME})}{(t\text{-BI-DME})} = \frac{k_3}{k_1}\left(\frac{k_2 + k_5 + k_6}{k_5}\right) = \frac{k_3}{k_1}\left(\frac{k_2}{k_5} + \frac{k_6}{k_5} + 1\right)$$

$$\text{and} \quad \frac{\text{(c-BI-DME)}}{\text{(t-BI-DME)}} = X\left(\frac{1}{W} + Z + 1\right)$$

The experimental ratio of oxetanes from c-DME is 0.617.

The oxetane steroselectivity relations yield two equations in two unknowns since cleavage to closure ratios, Y and Z, can be determined directly from product data. Thus, $Y = k_4/k_3 = 4.12$ is obtained from the ratio of "crossover" (c-DME/c-BI-DME) products resulting from addition to t-DME. Likewise, $Z = k_6/k_5 = 5.55$, obtained from the t-DME/t-BI-DME ratio for c-DME addition. Solving equations above for the remaining ratios W and X completes the determination of rate constant ratios shown in Table 5.

These ratios are computed from oxetane stereoisomer ratios and crossover product ratios where a true competition of cleavage, closure and bond rotation for the biradical mechanism must exist. A "check" on the completeness of the biradical scheme in rationalizing all of the limiting quantum yield data can be made with reference to the computed relative rates of cleavage, closure, and rotation and observed alkene ratios (Scheme 1).

For the combination of biacetyl and t-DME,

$$\frac{\text{t-DME}}{\text{c-DME}} = \frac{k_{6(TB)}}{k_{4(CB)}} = \frac{k_6}{k_4}\left(\frac{k_1 + k_3 + k_4}{k_2}\right) = \frac{k_6}{k_2}\left(\frac{k_1}{k_4} + \frac{k_3}{k_4} + 1\right)$$

$$= WZ\left(\frac{1}{XY} + \frac{1}{Y} + 1\right) = 3.31 \text{ (observed = 7.50)}$$

For the combination of biacetyl and c-DME

$$\frac{\text{c-DME}}{\text{t-DME}} = \frac{k_{4(TB)}}{k_{6(CB)}} = \frac{k_4}{k_6}\left(\frac{k_2 + k_5 + k_6}{k_1}\right) = \frac{k_4}{k_1}\left(\frac{k_2}{k_6} + \frac{k_5}{k_6} + 1\right)$$

$$= XY\left(\frac{1}{WZ} + \frac{1}{Z} + 1\right) = 0.462 \text{ (observed = 1.81)}$$

Table 5. Rate Constant Ratios for Biradical Dynamics (Scheme 2) Computed from Product Ratios for Biacetyl/dimethoxyethene Addition and Isomerization

Rate Constant Ratio	For Biradicals (TB)	For Biradicals (CB)
k (cleavage)/k(closure)	$Z = k_6/k_5 = 5.55$	$Y = k_4/k_3 = 4.12$
k (closure)/k (rotation)	$W = k_5/k_2 = 0.055$	$X = k_3/k_1 = 0.025$
k (cleavage)/k (rotation)	$k_6/k_2 = 0.305$	$k_4/k_1 = 0.103$

The quality of the kinetic analysis above depends of course on the experimental error of product ratios and quantum yields. Thus, the uncertainty in the ratio of oxetane stereoisomers (~20%, from each side) suggests a considerable range for the ratios, W and X, but leaves unaltered the result that rotation is much faster than closure. Experimental uncertainty associated with the ratio of crossover products will likewise allow variation of Y and Z but the favor for cleavage over closure will remain. Although the comparison of computed and observed alkene ratios depends on absolute quantum yields, we feel confident in claiming a high degree of stereoretention in bimolecular decay and an apparent discrepancy between stereochemical losses for oxetane formation and regeneration of alkene by the biradical mechanism.

The extent of anomalous alkene stereoretention in bimolecular decay can be further evaluated. From the calculated rate constant ratios and starting with t-DME, the predicted "yield" of t-DME is 35.5% (3.31 times the 10.7% cis component) leaving 0.645 as the expected sum of quantum yields of products from t-DME/biacetyl (observed = 0.21). Likewise biradicals should give only 14.9% (0.46 x 32%) c-DME suggesting a high quantum yield of products starting with c-DME, yet the sum of efficiencies for oxetane formation and isomerization is only 0.38. Large components of "stereospecific cleavage"[37]

are therefore calculated (from t-DME, 80.2 - 35.5 = 44.7% and from c-DME 58.4 - 14.9 = 43.5%).

The inclusive biradical mechanism in which all bimolecular decay is ascribed to biradical partitioning (shown in Scheme 3 for biacetyl and alkene) has been considered previously for ketone triplet quenching and cycloaddition but in general has not been favored. Wagner and Kochevar[19] have argued that interaction of ketone triplets and alkenes should be more responsive to steric effects than electronic factors (alkene donor properties) if radical addition to alkene is the correct model. This position is relevant to the biacetyl quenching results considering particularly the undiminished reactivity of relatively hindered alkenes TME and hexamethyldewarbenzene. The absolute rates of ketone triplet quenching were also judged[19] to be unsuitable for the radical addition model being some two to three orders of magnitude higher than rates expected for bimolecular reaction of radicals and alkenes ($k = 10^5 - 10^7$ M^{-1} sec^{-1} [39]). This argument seems appropriate for the more robust ketone triplets but is less confidently applied to biacetyl/alkene interactions. The quenching of biacetyl triplets is well within the range of rates for radical attack and biacetyl triplet could well be an exceptionally electrophilic radical.[40]

Scheme 3

BI	→	^{1}BI	excitation
^{1}BI	→	^{3}BI	intersystem crossing
^{3}BI	→	BI	triplet decay
^{3}BI + ALK	→	^{3}BR	biradical formation
^{3}BR	→	OX	oxetane formation
^{3}BR	→	BI + ALK	biradical decay

The foregoing analysis of biradical rate constant ratios assumes that the families of biradicals (CB and TB) achieve or nearly reach an equilibrium with respect to population of the subfamilies of s-cis and s-trans conformations (those shown in Scheme 2). Biradical cleavage, closure, and rotation do not truly compete if extended biradical rotamers never reach the gauche forms necessary for ring closure. Thus, the large component of stereoretaining bimolecular decay apparent in the quantum yield data might simply be the result of a preference for formation and relatively rapid cleavage of s-trans biradicals.

This position is not supported by the stereochemical data for oxetane formation which serves as an "internal standard" for the competitive position of biradical bond rotation rates. The nearly randomized stereochemistry observed for cycloaddition (the low closure/rotation ratios - Table 5) are most consistent with triplet biradical intermediates with lifetimes that are long with respect to rotation about single bonds. The stereochemical losses in oxetane formation are reconciled with alkene decay ratios only if a large barrier separates the subfamilies of extended and gauche biradical conformations, with the extended rotamers having a much shorter lifetime. The origin of such artifacts is not obvious even taking into account ponderal effects (particularly involving rotation at tertiary biradical centers[41]) which can reduce the competitive position of stereoequilibrating rotations.

A more satisfying picture is obtained if the previously discussed exciplex mechanism is invoked but including biradical intermediates. Reversible formation of an exciplex followed by biradical formation and partitioning accounts for (1) the structure-reactivity relationships for biacetyl triplet quenching (the result of polar exciplex binding), (2) quantum wastage (the preference for regeneration of unisomerized alkene through direct exciplex

decay), and (3) stereochemical losses in oxetane and recovered alkene (the result of biradical equilibration and decay). The mechanism is fully consistent with earlier results and proposals concerning alkene isomerization by the Schenck mechanism[36] and cycloaddition stereochemical results for ketone triplets[2e,35] and other systems.[17] Gupta and Hammond[36a] have provided evidence that the triplet exciplex precursor to biradicals in the acetophenone/2,2-dimethyl-3-hexene system can be intercepted by a secondary quencher. In addition, direct evidence for reversible formation of an (emitting) exciplex from the triplet of the dicarbonyl, benzil, and an electron donor, anisole, has been obtained.[42]

The exciplex/biradical mechanism for biacetyl triplet quenching, oxetane formation, and sensitized alkene isomerization is shown in Scheme 4. Steady state analysis gives the relationship below (eqn 8) for the quantum yield of oxetane formation where $P = k_5/k_5 + k_6 + k_7$

Scheme 4.

BI	$\xrightarrow{h\nu}$	^{1}BI		excitation
^{1}BI	$\longrightarrow$	^{3}BI		intersystem crossing
^{3}BI	$\longrightarrow$	BI	k_1	triplet decay
^{3}BI + ALK	$\rightleftharpoons$	EXC	k_2, k_{-2}	exciplex formation
^{3}EXC	$\longrightarrow$	^{3}BR	k_3	biradical formation
^{3}EXC	$\longrightarrow$	BI + ALK	k_4	exciplex decay
^{3}BR	$\longrightarrow$	OX (c + t)	k_5	oxetane formation
^{3}BR	$\longrightarrow$	BI + ALK	k_6	biradical decay
^{3}BR	$\longrightarrow$	BI + ALK_i	k_7	alkene isomer formation

A similar expression is derived for the quantum yield of alkene isomerization (where $P = k_7/k_5 + k_6 + k_7$). The intercept/slope ratios (for plots of $1/\phi_{ox}$ vs. 1/[ALK]) and their relationship to phosphorescence quenching constants and biacetyl triplet lifetime ($\tau_o = 1/k_1$) are shown in eqn 8-10.

$$\frac{1}{\phi_{ox}} = \frac{k_3 + k_4}{Pk_3} + \frac{(k_{-2} + k_3 + k_4)\, k_1}{Pk_2k_3(ALK)} \qquad (8)$$

$$\frac{i}{s} = \frac{k_2}{k_1}\left(\frac{k_3 + k_4}{k_{-2} + k_3 + k_4}\right) = k_q \tau_o \qquad (9)$$

$$k_q = k_2\left(\frac{k_3 + k_4}{k_{-2} + k_3 + k_4}\right) \qquad (10)$$

The expression for k_q (eqn 10) is equivalent to eqn 4 above. The linear relationship of $1/\phi_{ox}$ and 1/[AlK] is confirmed for biacetyl disapperance in the presence of indene and TME, and quenching constants (k_q) obtained from disappearance quantum yield plots and phosphorescence quenching compare favorably. Association of the triplet exciplex - biradical mechanism with formation of ene product (BI-TME) in common with oxetane formation (BI-IND and BI-DME) is warranted in view of results of the labeling study of biacetyl photoaddtion to α-methylstryrene.[2a]

Summary: Some Comparisons. The dominant mechanism for photoaddition of biacetyl and alkenes involves biacetyl triplets. Additional evidence of mechanism derives from the behavior of biacetyl/dimethoxyethene (DME). Losses of stereochemistry in oxetane photoadducts and in recovered alkene are observed, consistent with the intermediacy of triplet biradicals. A working hypothesis concerning biradical dynamics is presented in Scheme 2 with rate constant ratios extracted from stereochemical data as shown in Table 5. Polar exciplex precursors to biradicals are also indicated as intermediates from (1) the electron donor-acceptor nature of the structure-reactivity profile for biacetyl triplet quenching and (2) the differential pattern of losses of stereochemistry in oxetanes and in recovered alkene which requires the intervention of a bimolecular species capable of non-radiative decay to biacetyl and alkene without loss of stereochemistry.

An interesting profile of excited state structure, energetics, and reactivity is obtained from a comparison of data for biacetyl and its prototype partner, acetone. The spacing of n,π^* carbonyl excited states provides a definitive series (for acetone, E_S = 85 and E_T = 78 kcal/mol. and for biacetyl, E_S = 62 and E_T = 56 kcal/mol). Representative data for quenching of carbonyl emission are shown in Table 6. The principal trends are that singlets are more reactive than triplets and that this difference is more pronounced for biacetyl. The more effective singlet quenching is most likely the result of higher polarizability for singlets vs. triplets, and the absence of a spin restriction on radiationless decay for singlet excited complexes. The diffuse nature of n and π^* orbitals for the diketone enhances the polarizability difference between singlet and triplet excited states for the conjugated dicarbonyl.[43]

Table 6. Rate Constants for the Quenching of Ketone Emission by Alkenes[a]

Ketone	Quencher	k_q^1	k_q^3
acetone	2,3-dimethyl-2-butene	1.4×10^8	5.1×10^7 [b]
biacetyl	2,3-dimethyl-2-butene	4.0×10^6	1.5×10^5
acetone	1,2-dialkoxyalkene[b,c]	2.0×10^9	4.5×10^9
biacetyl	1,2-dialkoxyalkene[c]	3.4×10^9	5.0×10^7

[a]Rate constants in M^{-1} sec^{-1} for quenching room temperature fluorescence (k_q^1) and phosphorescence (k_q^3) in hydrocarbon solvent (except where noted). Data taken from ref 4a, 5, 12, 18, 35 d and this work. [b]Acetonitrile solvent. [c]cis-1,2-Diethoxyethene or cis-1,2-dimethoxyethene.

The diminished reactivity of the less energetic biacetyl triplet revealed in quenching rates is partially but not entirely reflected in reaction quantum yields (i.e., intermediates, albeit reluctantly formed, partition favorably in some cases). That excited biacetyl is a discriminating reagent is shown in the following examples. Biacetyl and TME give the ene adduct, BI-TME[2b], whereas acetone triplet -TME adducts consist of about equal amounts of ene and oxetane isomers.[35b] The addition of biacetyl to enol ethers[2b] is more regioselective than the corresponding reaction of triplet acetone.[14b] Reduced reactivity is also apparent for biacetyl singlets (beyond a diminished quenching ability). N-methylpyrrole (NMP) is an efficient quencher of both acetone and biacetyl singlets yet only acetone is successful in generating addition product, A-NMP (via an unstable oxetane adduct)[45,46]. Thus, the photoaddition chemistry of alkenes and the less energetic biacetyl excited species has reasonable generality but is not robust and appears to obey a "reactivity-selectivity principle"[47] in terms of product distributions (biradical decay) and absolute quantum yields (exciplex and biradical decay).

EXPERIMENTAL SECTION

Emission measurements were carried out using Hitachi MPF-2A or MPF-44A fluorescence spectrophotometers. A Varian Model 1400 gas chromatograph (FI detector, nitrogen carrier gas) was used for analytical glc measurements. Reagent grade benzene was purified by washing with sulfuric acid, aqueous solution carbonate and water followed by distillation of the dried benzene extract from sodium (middle cut). Commercially available quenchers were distilled under nitrogen (indene, under reduced pressure).

trans-1,2-Dimethoxyethene (t-DME). cis-1,2-Dimethoxyethene[48] was prepared from methoxyacetaldehyde dimethyl acetal (Aldrich) following the procedure of McElvain and Stammer[49] used for preparation of dimethoxyethene. A convenient photochemical procedure provided an alternative to the reported catalytic method for cis-trans isomerization of DME (a procedure which gives an equilibrium mixture that favors the cis isomer). A solution of 6 g (0.07 mol) of c-DME and 6 g (0.04 mol) of m-methoxyacetophenone in 270 ml of benzene was photolyzed for four hours in a standard immersion well equipped with a 450 W medium pressure mercury lamp and Pyrex filter. Glc analysis showed an 80% conversion to t-DME. The solvent was removed in vacuo, and the resulting mixture was separated by preparative glc (column A: 20% Carbowax 20M on 60-80 Chrom W, 6 ft x 3/8 in). The relative retention time of the isomers is 1.4/1 (c/t). Pure t-DME (1.5 g, 25% yield) displays the following nmr spectrum[48] (CCl_4): 3.3 (6H, s, -OMe) and 6.1 (2H, s, vinyl H) (the cis isomer displays signals at 3.1 and 5.1 δ ppm. The purity of stereoisomers of DME obtained by these methods was greater than 99% (glc).

Preparation of Oxetanes. Photoaddition of biacetyl to furan,[2b] indene[2b], and 2,5-dimethyl-2,4-hexadiene (DMH)[5] was carried out using procedures similar to those reported. The adducts of biacetyl and dimethoxyethene were prepared

as follows. A solution of 2 g (0.02 mol) of biacetyl and 2 g (0.02 mol) of c-DME in 270 ml of spectrograde acetonitrile was photolyzed for 17 hr with a 450 W Hanovia medium pressure mercury lamp (uranium glass filter, > 340 nm) with continuous nitrogen purging. A small amount of sodium carbonate was added to the solution to prevent acid catalyzed decomposition of photoproduct.[14b] Solvent and unreacted addends were removed in vacuo after photolysis giving 3 g of a crude product which was purified by preparative glc (Column A). The chromatogram consisted (cleanly) of two peaks in a 2:1 ratio. The shorter retention time (8 min, 130°) major product (0.77 g collected) assigned the structures, t-BI-DME, had the following properties including a resolution in the nmr spectrum of two components in an apparent ratio of 8:1.

Ir (CCl_4): 2920, 1720, 1080, and 1170 cm^{-1}

Nmr (CCl_4): (major component) 1.3 (3H, s, $-CH_3$), 2.2 (3H, s, $-COCH_3$), 3.3 (3H, s, $-OCH_3$), 3.4 (3H, s, $-OCH_3$), 3.8 (1H, d, J = 3 Hz, β ring hydrogen), and 5.0 (1H, d, J = 3 Hz, α ring hydrogen) δ ppm; (minor component) 1.4 (3H, s, $-CH_3$), 2.3 (3H, s, $-COCH_3$), 3.6 (1H, d, J = 3 Hz, β ring hydrogen), and 5.15 (1H, d, J = 3 Hz, α ring hydrogen) δ ppm (methoxy group signals not well resolved for minor component).

Anal: C,H.

The longer retention time (16 min, 130°) minor product (0.30 g collected), assigned the structures, c-BI-DME, displayed properties similar to the major adduct including the appearance in the nmr spectrum of two components (10:1).

Ir (CCl_4): 2920, 1720, and 1100 cm^{-1}.

Nmr (CCl_4): (major component) 1.4, 2.2, 3.3, 3.4, 4.1, and 5.2 δ ppm; (minor component) 1.45, 2.3, 3.9, and 5.35 δ ppm (assignments in the order given above): for doublets at 3.9, 4.1, 5.2, and 5.35, J = 5 Hz .

Anal: C,H.

Emission Measurements. The fluorescence of aerated 0.05 - 0.1 M solutions of biacetyl was monitored at 480 nm in Pyrex cells (excitation at 422 nm). The observation of biacetyl phosphorescence[6] required the degassing of samples in cells equipped with ground glass joints for vacuum line connection (three freeze-pump-thaw cycles). Alternatively, biacetyl phosphorescence was observed from samples fitted with a serum cap and syringe needles for nitrogen purging. The reduction of fluorescence or phosphorescence on the introduction of quenchers was analyzed using the Stern-Volmer equation, $I_o/I = 1 + K_{sv}[Q]$ where I_o,I are emission intensities without and with quencher and K_{sv} is the Stern-Volmer constant = $k_q\tau_o$. A linear least squares program was used to compute the slopes and intercepts of Stern-Volmer plots. Calculated standard deviations were 5% for fluorescence measurements (8-10 points) and 20-30% for phosphorescence quenching (4-6 points).

Quantum Yield Determinations. Solutions (5 ml) containing 0.1 or 0.5 M biacetyl in benzene and varying concentrations of the addends in 15 x 1.5 cm Pyrex cylindrical tubes were degassed by passing dry nitrogen through syringe needles inserted through rubber serum caps. Tubes were photolyzed in a Rayonet RPR-204 photochemical reactor equipped with a merry-go-round apparatus as described previously.[51] The equipment allowed parallel irradiation of biacetyl solutions with varying concentrations of addends and of actinometer solutions for absolute quantum yield measurements. Valerophenone in benzene with dodecane as internal standard was the actinometer (g/c analysis on column B: 5% FFAP, on 60-80 mesh Chrom W, 8 ft x 1/8 in), the conversion to acetophenone was assumed to have a quantum yield of 0.33.[52] Differential absorption by biacetyl and valerophenone over the emission profile of the Rayonet RUL 3500 lamps was accounted for using procedures previously described.[53]

Biacetyl disappearance on photolysis in the presence of indene, furan, and tetramethylethylene was monitored spectrophotometrically at 422 nm. Photolysis

was limited to 20-30% conversion. Duplicate measurements showed an average deviation of < 20%. Photoproducts from the irradiation of biacetyl and DME were monitored by flame glc (column B: 20% Carbowax 20 M on 60-80 mesh KOH-washed Chrom P, 10 ft x 1/8 in). Formation of c- and t-DME and c-BI-DME and t-BI-DME was measured vs. an internal standard, dodecane (peak areas corrected for detector response) and conversion to product was limited to < 5%.

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(22) Linear free energy relationships for quenching rate constants (IP plots and the like are increasingly common and found under circumstances for which the assignment of an outright electron transfer to the quenching mechanism is questionable and use of eqn 3 does not have a precise meaning For most combinations of organic neutrals the "extent of electron transfer" (f_{ct}) is small (even in polar solvents). For quite a range of electron donor-acceptor ability in potential exciplex pairs, electron transfer (formation of radical-ions) is not in evidence and in fact not expected on energetic grounds, and quenching rate constants show a modest dependence on solvent polarity. Exciplex formation and the redistribution of electron density in electron donor-acceptor pairs is the result of a complicated set of intermolecular forces,[23] some of which have to do with the mutual polarizability of exciplex participants, thus the correlation with redox thermodynamic parameters.

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(24) In energy units ($\Delta E = 2.3\ RT\ \Delta \log k_q$) the difference in rate constants for two alkenes for biacetyl quenching (1-phenylpropene vs. TME, $\Delta IP = 0.14$) is 0.05 eV (1.2 kcal/mol) whereas for biacetyl vs. benzophenone ($\Delta E_T + \Delta E_{red} = 0.1$) quenching by TME, the energy equivalent is 0.22 eV (5.2 kcal/mol) (T = 298 K).

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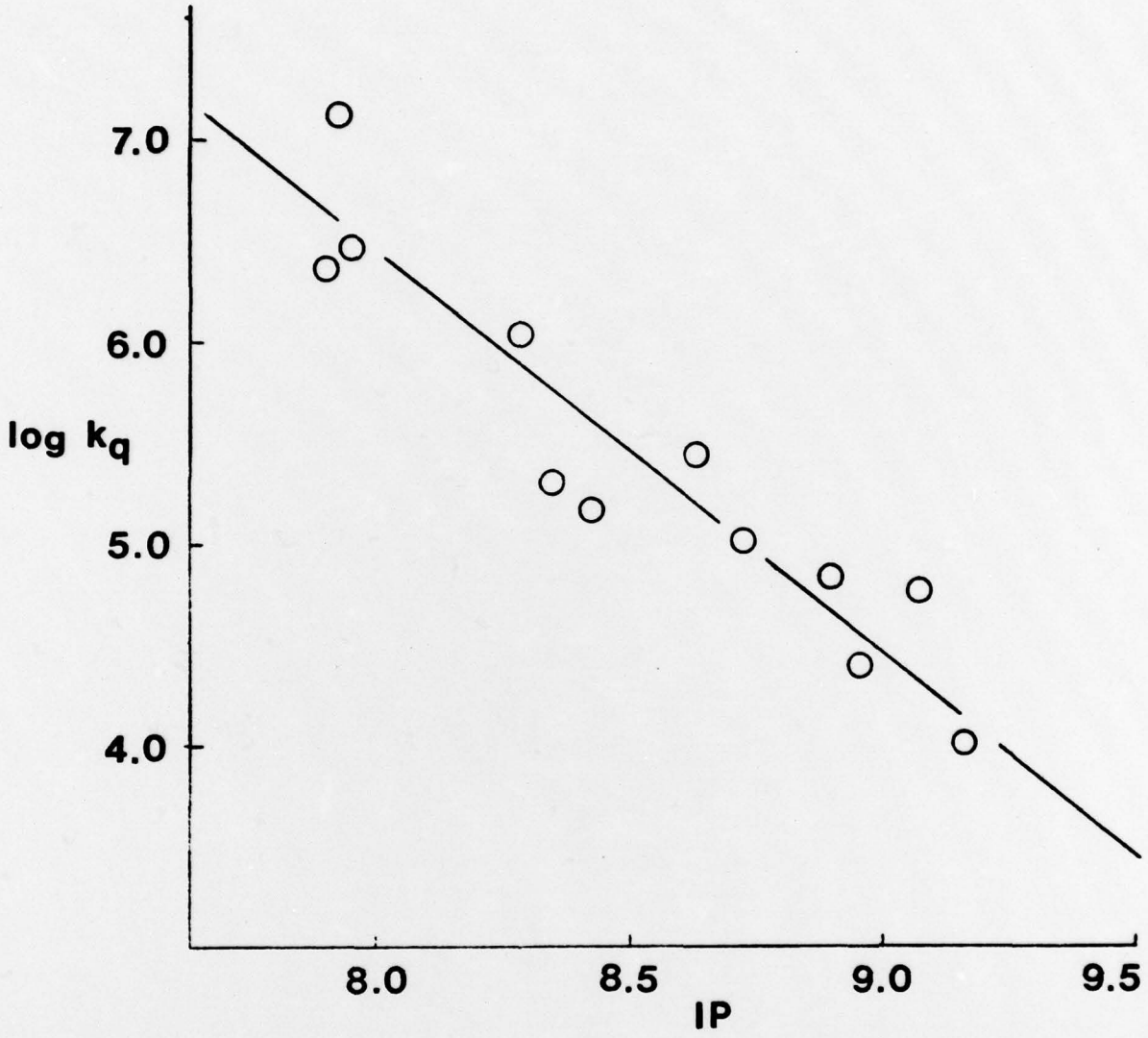


Figure 1. Dependence of rate constants for the quenching of biacetyl phosphorescence on the ionization potential (eV) of alkene quenchers

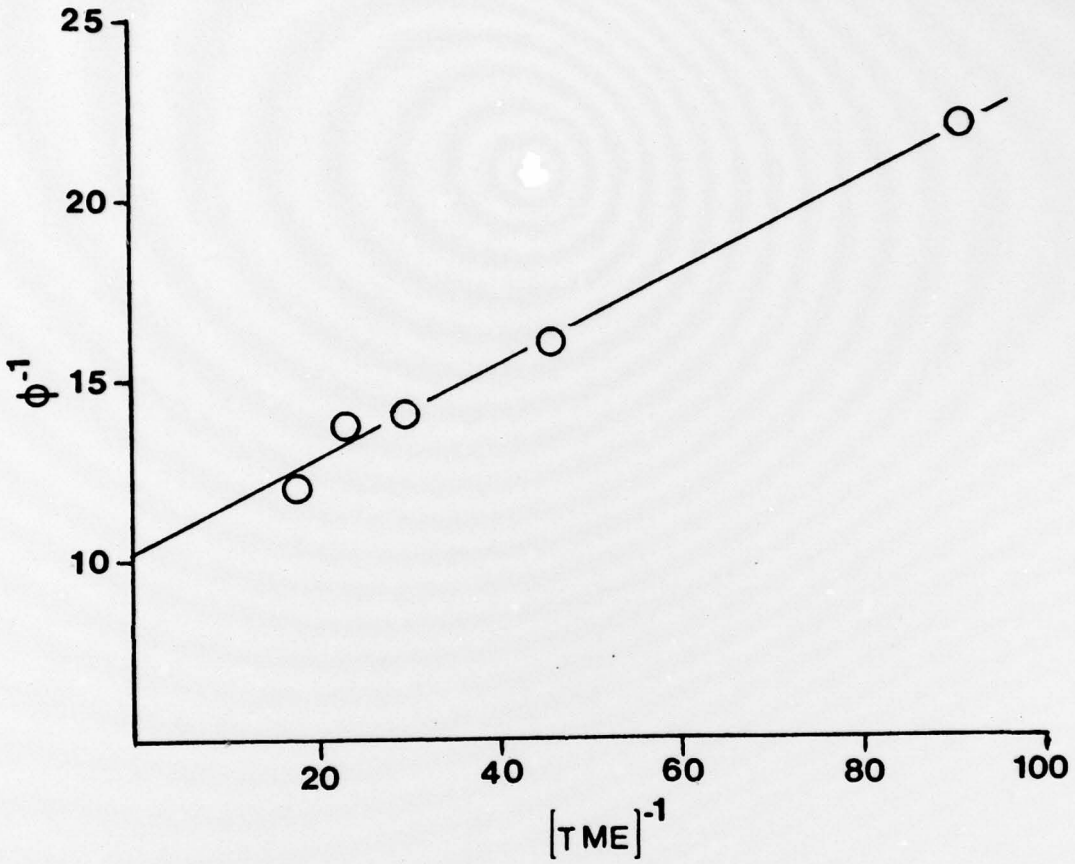


Figure 2. The dependence of quantum yield for disappearance of biacetyl in benzene on the concentration of tetramethylethylene (TME)

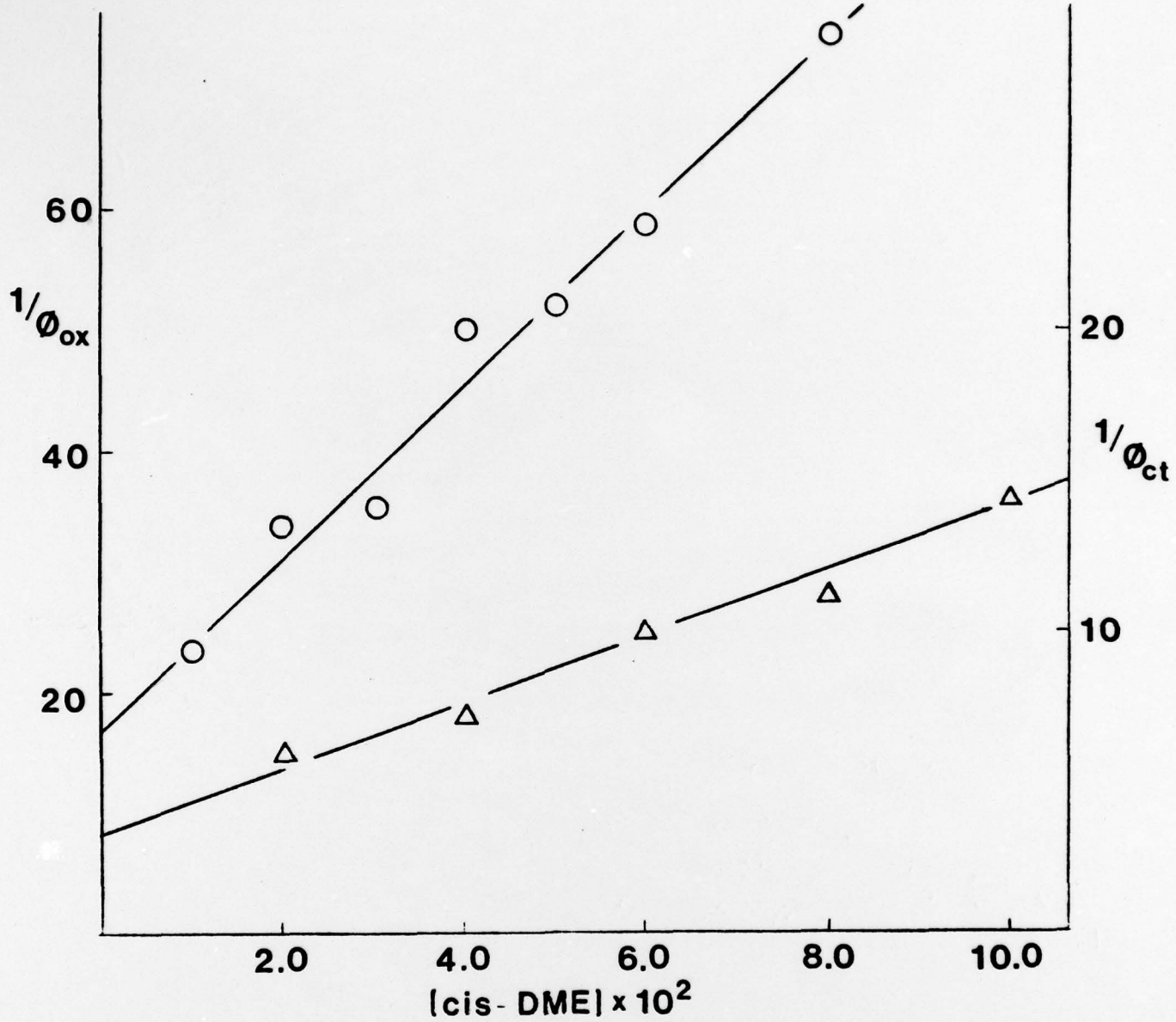


Figure 3. The concentration dependence of reciprocal quantum yields for oxetane formation (O , left ordinate) and trans-cis isomerization (Δ , right ordinate) of biacetyl and cis-dimethoxyetheene (c-DME) in benzene

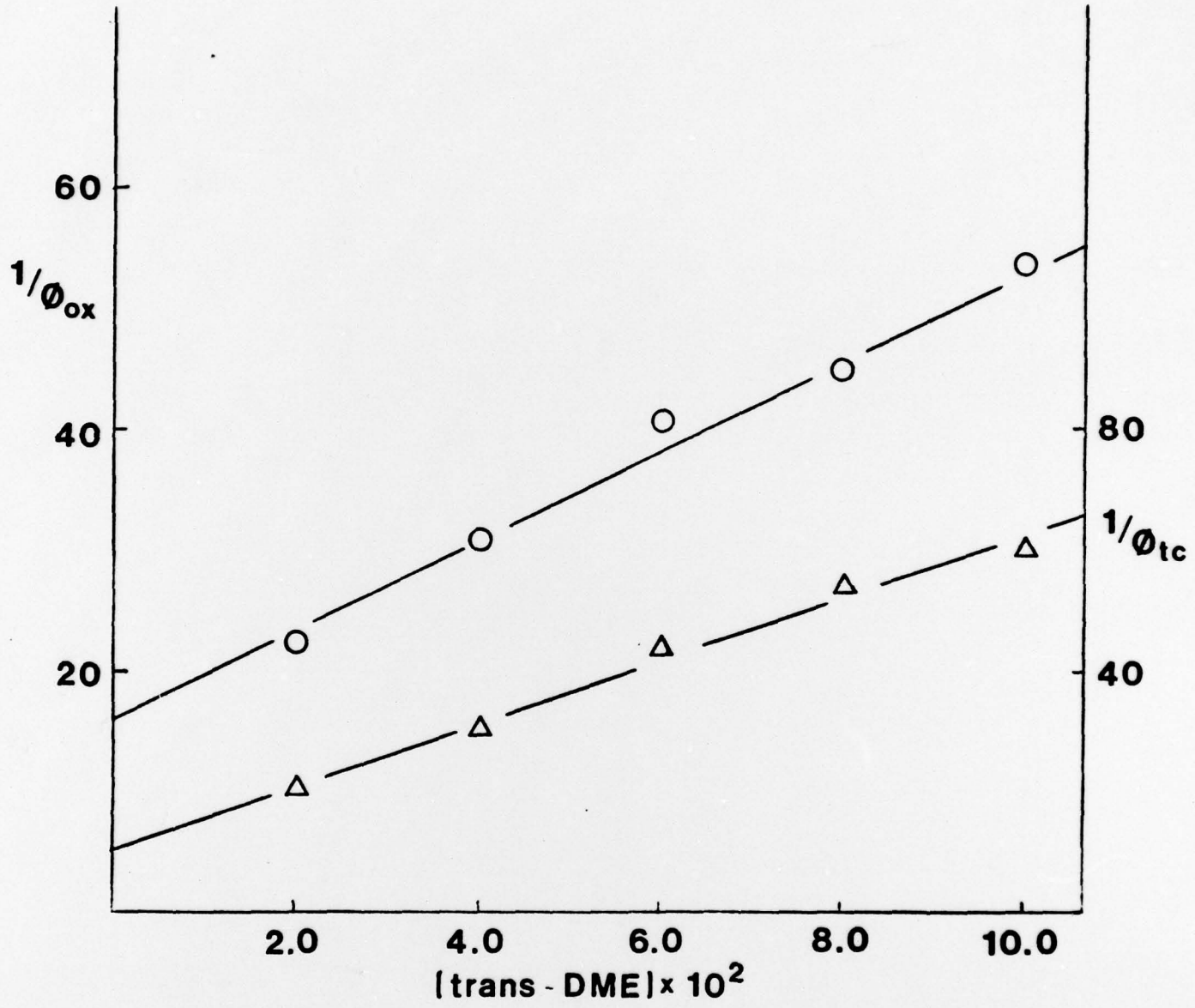
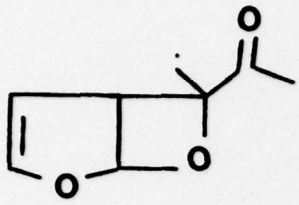
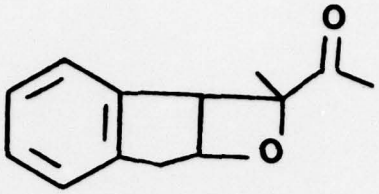


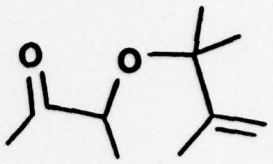
Figure 4. The concentration dependence of reciprocal quantum yields for oxetane formation (O, left ordinate) and trans-cis isomerization (Δ, right ordinate) of biacetyl and trans-dimethoxyethene (t-DME) in benzene



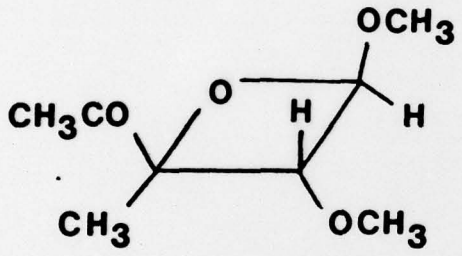
BI-FUR

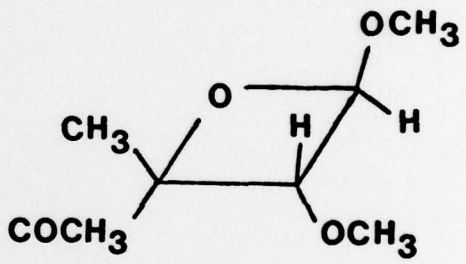


BI-IND

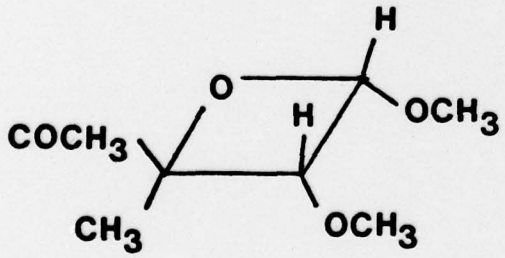


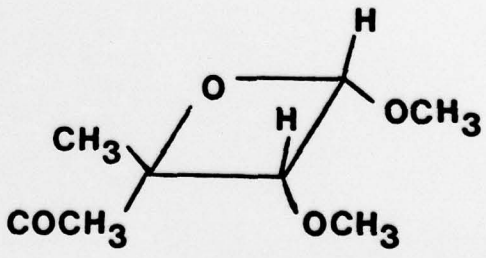
BI-TME



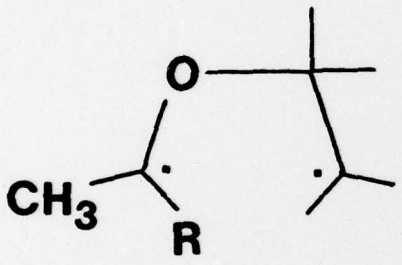


t-BI-DME

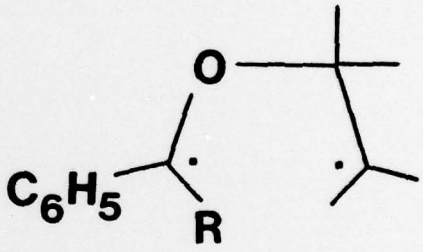




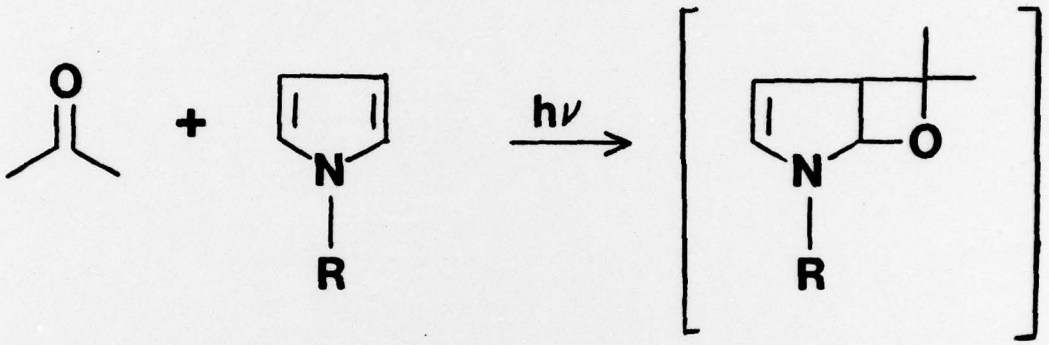
c-BI-DME

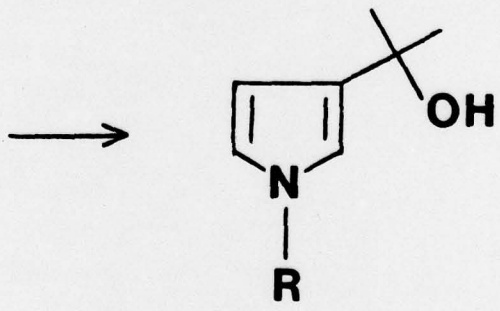


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